NATURE OF CEMENTING MATERIALS IN ORTSTEIN HORIZONS OF SELECTED FLORIDA SPODOSOLS

BY

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Five pairs of ortstein and non-ortstein profiles of Aquods were studied in an attempt to identify the nature of cementing materials. Ortstein clods did not collapse in water, while dithionite-citrate was the most effective slaking reagent. Quartz, gibbsite, kaolinite, and hydroxy-Al interlayered vermiculite were dominant clay minerals. The ortstein horizons had significantly larger amounts of dithionite-citrate-extractable Al, significantly higher silt plus clay contents, and significantly higher bulk density than did non-ortstein spodic horizons. Moist and air-dried ortstein samples had similar shear strengths, but the strength significantly decreased by 14 to 82% for oven-dried samples. The strength had a significant correlation with the dithionite-citrate-extractable Al. Energy-dispersive spectra showed that Si and Al were major constituents of both

ortstein and non-ortstein samples. However, ortstein samples had stronger Al peaks. More gel-like materials and fine particles were observed in the pore space of ortstein than non-ortstein samples in scanning electron micrographs. Cracks of dry gel-like substances between coarse particles were also observed. Electron-dot pictures revealed that gel-like substances were Al-dominated. Results of chemical analyses suggested that they were predominantly Al-fulvate.

Neighboring ortstein and non-ortstein samples from Alachua County were studied to find possible sources of Al and fulvic acids accumulated in ortstein horizons. Extractable Al and fulvic-acid contents were significantly lower in surface horizons and significantly higher in spodic horizons at ortstein sites than in corresponding horizons at non-ortstein sites suggesting that more intense leaching had occurred in the ortstein area. Differences between ortstein and non-ortstein spodic horizons in both Al and fulvic-acid contents were much higher than those between surface horizons. Following a topographic difference, Al and fulvic-acid contents in Bh horizons increased from northeast to southwest, and then decreased. A similar trend was observed for the formation and disappearance of ortstein. These observations suggest that Al and fulvic acids might also have originated from seepage, translocated as Al-fulvate to the spodic horizons, and cemented the soil particles to form ortstein as a result of topographic differences.

CHAPTER I
INTRODUCTION

The word ortstein was first introduced in the soil literature in 1862. Since then, it has been used to designate a wide range of cemented soil materials (Muir, 1961; Wang et al., 1978). However, ortstein is now specifically defined as a cemented spodic horizon in Spodosols (Soil Survey Staff, 1975).

Ortstein had been found and studied in several countries, including Australia, Canada, Great Britain, and the United States. Organic matter, silica, non-crystalline Al silicates, Mn oxides, and oxides or hydroxides of Al and Fe have been suggested as cementing agents in cemented soils (Polteva and Sokolova, 1967; Karavayeva, 1968; Flach et al., 1969; McKeague and Wang, 1980; McKeague and Kodama, 1981; Farmer et al., 1984). The cementation is usually too hard to be penetrated by roots. Its presence is also associated with low pH, low CEC, low exchangeable bases, and low permeability (Lambert and Hole, 1971; McKeague and Sprout, 1975; Moore, 1976; Miles et al., 1979). This combination of properties limits the use of such soils for forestry and agriculture purposes.

There are about 6 million hectares of Spodosols in Florida (Carlisle and Brown, 1982). Ortstein horizons are found in many of them. However, little is known about the nature of the cementing materials which contribute to their formation. A series of experiments was devised to identify possible cementing agents and their translocation to ortstein horizons, and to study morphological, chemical, physical, and mineralogical properties of Florida ortstein and non-ortstein soils. The genesis of ortstein horizons in Alachua Spodosols will also be postulated.

CHAPTER II
LITERATURE REVIEW

Environmental Factors Conductive to Ortstein Formation

Climate

Temperature is not a restricted factor of ortstein formation. The horizon has been found in cold, cool, and warm areas with mean annual soil temperature of 0°C (Polteva and Sokolova, 1967; Moore, 1976), 5-10°C (McKeague and Sprout, 1975), and higher than 22°C (Carlisle and Brown, 1982) but only in humid areas with alternate wet and dry periods (Polteva and Sokolova, 1967; Karavayeva, 1968; McKeague and Sprout; 1975; Wang et al., 1978). Under such conditions, active amorphous materials composed of organic matter, Al and/or Fe or Mn may be moved in wet season by percolating water and accumulated in the spodic horizon to form ortstein (Soil Survey Staff, 1975; Boul et al., 1980). In addition, elements such as Fe and Mn may become mobile in the reduction period and precipitate in the oxidation period (Polteva and Sokolova, 1967).

Vegetation

Types of vegetation and litter are important for the development of ortstein horizons. The typical vegetation is either broadleaf or coniferous forest or a mixture of these, such as spruce mixed with aspen and birch (Polteva and Sokolova, 1967), spruce mixed with fir and jack pine (Moore, 1976; Wang et al., 1978; Arshad and St. Arnaud, 1980) and Hill's oak mixed with jack pine (Lambert and Hole, 1971). Canopy drip and litter leachate from these trees are acidic and contain effective chelating agents. They speed the weathering of surface minerals and complex with the weathered products to form soluble organo-metallic compounds which accumulate as cementing agents in spodic horizons.

Relief

Ortstein areas studied in several countries are characterized by a slightly hilly relief (Polteva and Sokolova, 1967; McKeague and Sprout, 1975; Wang et al., 1978). Relief favors the formation of ortstein horizons probably due to lateral inflow of soluble metallic or organo-metallic compounds with the groundwater into soils of subordinate positions suggested by Polteva and Sokolova (1967).

Parent Materials

Although ortstein horizons have been found in areas with fine-textured parent materials (Polteva and Sokolova, 1967), they form mostly in the areas with coarse-textured parent materials (Lambert and Hole, 1971; McKeague and Sprout, 1975; Moore, 1976; Wang et al., 1978; Arshad and St. Arnaud, 1980). The latter are conducive to the processes of ortstein formation including weathering, leaching, and accumulation of cementing materials (Soil Survey Staff, 1975).

Time

By determination of Mean Residence Time (MRT) with ^{14}C, De Coninck (1980) found that the ortstein horizon in his study had a MRT of ±2100 years and the non-ortstein horizon ±180 years. Based upon the findings that very weak cementation occurred at sea level and strong cementation 20 m above that level, Moore (1976) suggested that this difference was an indication of the rates of soil formation. By using radiocarbon dating of organic matter, he suggested that 5000-6000 years were required for the development of the ortstein horizons investigated.

Properties of Ortstein Horizons

The degree of cementation and the properties of individual ortstein horizon vary considerably depending on mineralogical and chemical composition of cementing materials. Properties of ortstein horizons may be summarized as follows.

Morphological Characteristics

Ortstein horizons may occur in many soil types. In Canada, they are massive and continuous in poorly drained soils and discontinuous in well to imperfectly drained soils (Wang et al., 1978). The color of ortstein horizons from various areas differs because of differences in chemical compositions. Oxides and hydrous oxides of Fe may impart a reddish brown color (Arshad and St. Arnaud, 1980). The existence of organic matter or Mn oxides may result in dark or black colors depending on their amounts (Lambert and Hole, 1971; McKeague and Sprout, 1975; Moore, 1976; Wang et al., 1978). The upper boundary of ortstein horizons is usually abrupt, while the lower one may be abrupt or diffuse (Polteva and Sokolova, 1967; McKeague and Sprout, 1975; Wang et al., 1978). The horizon is generally too hard to be penetrated by roots (Polteva and Sokolova, 1967; McKeague and Sprout, 1975).

Chemical Properties

The horizons were moderately to extremely acidic and low in exchangeable bases (Sokolova and Polteva, 1968; McKeague and Sprout, 1975; Moore, 1976; Miles et al, 1979; McKeague and Kodama, 1981). The ortstein clods did not slake in water, but slaked to a degree in Pyrophosphate and completely in dithionite-citrate, acid NH_4-oxalate, and 0.5 M NaOH solutions (McKeague and Sprout, 1975; Miles et al., 1979). Organic C was usually higher in ortstein than in other horizons or in non-ortstein counterparts (Sokolova and Polteva, 1968; McKeague and Sprout, 1975; Moore, 1976; Miles et al., 1979; Arshad and St. Arnaud, 1980). Although aluminum is generally the dominant cementing element, Fe and Mn have also been found important in cementation (Polteva and Sokolova, 1967; Karavayeva, 1968; Flach et al., 1969; Mckeague and Sprout, 1975; Babanin et al., 1976; Moore, 1976; Miles et al., 1979; Arshad and St. Arnaud, 1980). In the ortstein samples with high exchangeable Al, cation exchange capacity at pH 7 was markedly high (McKeague and Sprout, 1975; Moore, 1976; Miles et al., 1979).

Physical Properties

The sand content of most ortstein horizons was more than 50% and might go up to more than 90% (Moore, 1976;

Wang et al., 1978). Bulk density values were generally higher in ortstein than non-ortstein and other horizons (McKeague and Sprout, 1975; Wang et al., 1978). Ortstein horizons usually have the lowest hydraulic conductivity in a profile (Lambert and Hole, 1971; Wang et al., 1978). Shear strength of replicate ortstein clods varies appreciably. Wang et al. (1978) reported that the average shear strengths of 2.5 x 2.5 x 2.0 cm^3 clods ranged from 2.3 to 23 kg/cm^2 and usually exceeded 5.0 kg/cm^2.

Clay Mineralogy

Quartz and feldspar have been found to be the most abundant components in the clay fraction. Kaolinite, 2:1 minerals as vermiculite and chlorite, and/or hydroxy-Al interlayered minerals also existed. No significant difference in clay mineralogy was observed between ortstein and their non-ortstein counterparts (McKeague and Sprout, 1975; Miles et al., 1979).

CHAPTER III
MORPHOLOGY OF SPODOSOLS STUDIED

Introduction

The presence of a spodic horizon, with illuvial accumulation of organic matter, Al, and/or Fe, is a unique feature of Spodosols (Soil Survey Staff, 1975; Boul et al., 1980). The Spodosols used in this study came from central and north-central Florida. They are Haplaquods and occur in wet places having either humid climate and/or shallow fluctuating ground water. Their spodic horizons are principally an accumulation of organic matter and Al, while Fe and Mn are present in very small amounts (Soil Survey Staff, 1975). The purpose of this section is to report detailed morphological data of these Spodosols.

Sample Collection

Samples were collected from five counties in north-central and central Florida (Fig. 3-1). Paired Spodosol pits were opened in each county, one with and the other without a discernible ortstein horizon. The two pits were located

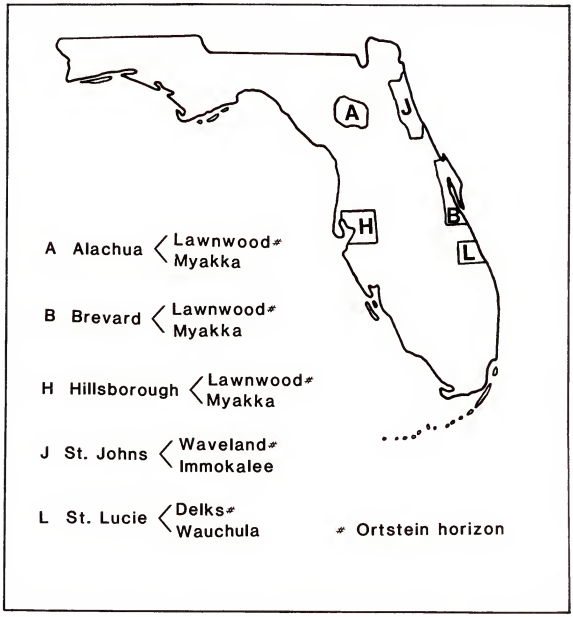


Fig. 3-1. Florida map showing the five sampling counties and the classification of soils sampled.

100-200 m from each other except in St. Lucie County, where they were about 1.6 km apart.

Ortstein horizons from Alachua, Brevard, and St. Lucie Counties could be divided into two layers according to the difference in color. The upper layer was black (10YR 2/1) and the lower layer was dark reddish-brown (5YR 3/3). Those from the other two counties were uniformly black (10YR 2/1).

Soil Environment and Classification

The soils studied belonged to six series. Three had an ortstein horizon, Delks (Sandy, Siliceous, Hyperthermic, Ortstein, Ultic Haplaquods), Lawnwood (Sandy, Siliceous, Hyperthermic, Ortstein, Arenic Haplaquods), and Waveland (Sandy, Siliceous, Hyperthermic, Ortstein, Arenic Haplaquods). The spodic horizons of the other three were non-ortstein. They were Immokalee (Sandy, Siliceous, Hyperthermic, Arenic Haplaquods), Myakka (Sandy, Siliceous, Hyperthermic, Aeric Haplaquods), and Wauchula (Sandy, Siliceous, Hyperthermic, Ultic Haplaquods) series (Fig. 3-1). Slash pine, wiregrass, and palmetto were typical vegetation. No distinct difference was observed between the vegetation of ortstein and that of non-ortstein areas.

The represented profiles of paired ortstein and non-ortstein Spodosol are described as follows.

Delks Series (St. Lucie County; Ortstein Profile)

Horizon	Depth (cm)	Description (Moist Colors)
A	0-18	Grayish brown (10YR 6/3) sand; weak, medium, granular structure; friable; few fine and many medium roots; very strong acid; clear smooth boundary.
E	18-51	Light reddish brown (5YR 6/3) sand; single grained; loose; common medium roots; extremely acid; irregular boundary.
Bh	51-56	Very dark gray (5YR 3/1) sand; weak, coarse, subangular blocky structure; firm; weakly cemented; many medium and large roots; very strong acid; clear wavy boundary.
Bhm1	56-75	Black (10YR 2/1) sand; common, medium, distinct, dark-brown (7.5 YR 3/2) and yellowish-red (5YR 5/6) mottles; moderate, medium subangular blocky structure; very firm; strongly cemented; very strongly acid; clear wavy boundary.
Bhm2	75-86	Dark reddish brown (5YR 3/3) sand; moderate, medium, subangular blocky structure; very firm; strongly cemented; very strongly acid; gradual wavy boundary.

E'	86-102	Pinkish gray (5YR 6/2) sand; single grained; loose; very strongly acid; gradual wavy boundary.
Btg	102+	Light brownish gray (10YR 6/2) sandy loam; common, medium, distinct, reddish-yellow (7.5 YR 6/8) mottles; moderate, medium, subangular blocky structure; firm; very strongly acid.

Immokalee Series (St. Johns County; Non-ortstein Profile)

Horizon	Depth (cm)	Description (Moist Colors)
A	0-15	Gray (5YR 5/1) sand; weak fine granular structure; very friable; many fine and medium roots; extremely acid; clear smooth boundary.
E	15-86	Pinkish gray (5YR 7/2) sand; single grained; loose; many fine and medium roots; very strongly acid; abrupt wavy boundary.
Bh	86-109	Black (5YR 2.5/1) sand; single grained; loose; sand well coated with organic matter; many fine and medium roots; extremely acid; clear wavy boundary.
C	109-137+	Pinkish gray (5YR 6/2) sand; single grained; loose; extremely acid.

Lawnwood Series (Hillsborough County; Ortstein Profile)

Horizon	Depth (cm)	Description (Moist Colors)
A	0-15	Gray (10YR 5/1) sand; weak fine granular structure; very friable; many fine and medium roots; very strongly acid; clear smooth boundary.
E	15-69	Pinkish white (7.5YR 8/2) sand; single grained; loose; few fine roots; slightly acid; abrupt wavy boundary.
Bh	69-71	Black (7.5YR 2/0) loamy sand; massive in place, crushes to moderate medium subangular blocky structure; firm; weakly cemented; few fine and medium roots; very strongly acid; clear wavy boundary.
Bhm	71-99	Black (10YR 2/1) loamy sand; common medium distinct dark brown (10YR 3/3) mottles; massive in place, crushes to weak medium subangular blocky structure; cemented in most parts; very firm, firm in parts; very few fine roots; extremely acid; gradual wavy boundary.
C	99+	Dark brown (7.5YR 3/2) sand; weak fine granular structure; very friable; very strongly acid.

Myakka Series (Alachua County; Non-ortstein Profile)

Horizon	Depth (cm)	Description (Moisture Colors)
A	0-20	Very dark gray (10YR 3/1) sand; weak medium granular structure; very friable; many fine, medium, and large roots; extremely acid; clear smooth boundary.
E	20-51	Gray (10YR 5/1) sand; single grained; loose; many fine and medium and few large roots; extremely acid; clear wavy boundary.
Bh	51-66	Very dark brown (10YR 2/2) sand; moderate medium granular structure; friable; many fine and medium roots; extremely acid; clear wavy boundary.
C	66-89+	Brown (10YR 5/3) sand; single grained; loose; very few roots; very strong acid.

Wauchula Series (St. Lucie County; Non-ortstein Profile)

Horizon	Depth (cm)	Description (Moist Colors)
A	0-15	Gray (10YR 5/1) sand; weak fine granular structure; very friable; many fine and medium roots; very strongly acid; clear wavy boundary.

E	15-56	Pink (7.5YR 8/4) sand; single grained; loose; few fine and many medium roots; medium acid; abrupt wavy boundary.
Bh	56-71	Black (7.5YR 2/0) sand; moderate medium granular structure; friable; few big roots; strongly acid; clear wavy boundary.
Btg	71+	Very dark brown (10YR 2/2) sandy loam; common fine distinct yellowish-brown (10YR 5/6) mottles; weak medium subangular blocky structure; friable; strongly acid.

Lawnwood Series (Alachua County; Ortstein Profile)

Horizon	Depth (cm)	Description (Moist Colors)
A	0-30	Very dark gray (10YR 3/1) sand; weak fine granular structure; loose; many fine, medium, and large roots; extremely acid; clear smooth boundary.
E	30-61	Light gray (10YR 7/1) sand; single grained; loose; many fine and medium and few large roots; strongly acid; gradual wavy boundary.
Bh1	61-91	Very dark gray (5YR 3/1) sand; single grained; few tongues of E materials, up to 8 cm in diameter; loose; extremely acid; clear wavy boundary.

Bh2	91-107	Black (5YR 2.5/1) sand; massive parting to moderate medium granular structure; cemented in few parts; firm in parts; extremely acid; clear wavy boundary.
Bhm1	107-122	Black (10YR 2/1) sand; weak medium subangular blocky structure; cemented in most parts; very firm, firm in parts; few fine and medium roots; extremely acid; gradual wavy boundary.
Bhm2	122-137	Dark reddish brown (5YR 3/3) sand; weak medium subangular blocky structure; cemented in most parts; very firm, firm in parts; few fine roots; extremely acid; clear wavy boundary.
C	137+	Yellowish brown (10YR 5/6) sand; single grained; loose; very strongly acid.

CHAPTER IV
ELECTRON MICROPROBE AND RELEVANT CHEMICAL AND PHYSICAL STUDIES OF CEMENTING MATERIALS IN ORTSTEIN HORIZONS

Introduction

Methods for chemical differentiation have been widely used in the study of ortstein materials. Although several reagents have been proposed for differentiating and identifying possible cementing materials, they often lack specificity (Norrish, 1975; Rendell and Batley, 1980). Other methods such as microscopic analysis may allow us to study the constituents involved without modifying the cemented structure (Qureshi et al., 1969; Norrish, 1975; De Coninck, 1980; McKeague and Wang, 1980; McHardy and Robertson, 1983; Lee and Kittrick, 1984).

In this study electron-microprobe analysis and relevant physical and chemical properties were employed in an attempt to identify possible cementing agents in Florida ortstein horizons.

Materials and Methods

Soils used were ortstein and non-ortstein samples taken from five counties in Florida as described in Chapter III.

Large blocks of ortstein samples were cut into 2.5 x 2.5 x 5.0 cm^3 clods which were used for the determination of shear strength at different moisture levels (field moist, air-dried, and oven-dried at 105°C for 24 h) by unconfined compression tests (Das, 1982). The specimens were taken from the same ortstein blocks whenever possible, to reduce variability. Some ortstein blocks and samples of non-ortstein spodic horizons were cut into 2.5 x 2.5 x 2.5 cm^3 cubes for bulk density determination by the clod method (Blake, 1965).

For determinations of dithionite-citrate-extractable Al, Si, and Fe (Scheldrick, 1984; Table 4-1) and of particle-size distribution, samples of ortstein and non-ortstein spodic horizons were air-dried, crushed, mixed, and sieved to remove coarse fragments (>2 mm). The dithionite-citrate reagent was chosen for the extraction because it was the most effective among commonly used reagents in causing structural collapse of ortstein clods (Chapter V). Therefore, Al, Si, and Fe extracted by this reagent may be related to the cementation.

To eliminate possible variation introduced by separate samples, the relationship between shear strength and

extractable Al (Table 4-3) was studied using samples for extractable Al analyses from collapsed clods in the shear strength determination. Correlation coefficient (r) was used to show the statistical differences (Table 4-3) between shear strength and extractable Al and Fe.

For particle-size distribution, 100 g soil samples (<2 mm) were pretreated with 30% H_2O_2 to remove organic matter. After the digestion was completed, the digests were boiled to remove excess H_2O_2 and the supernatant solutions were discarded. After leaving overnight in an 100 ml 5% Calgon solution, the samples were mixed with a soil mixer, transferred into 1000 ml beakers, shaken, and placed into water bath (25°C). The separation of sand, silt, and clay was made following the procedure outlined by Day (1965).

For electron microprobe analysis, undisturbed clods from ortstein and non-ortstein spodic horizons were dried in an oven at 105°C for 24 h so that they could be successfully impregnated with epoxy resin. After hardening, the surface of each sample was ground and polished with 5 and 1 μ DuPont diamond paste. The samples then were examined using a JEOL Superprobe 733 microprobe. Operating conditions and limits of detection were similar to what was reported by Lee and Kittrick (1984). During the grinding process, thin layers of cementing materials might have been removed and might not be detected by the electron beam due to the limited depth of beam penetration.

To test whether dithionite-citrate-extractable Al and average silt plus clay contents were significantly different between ortstein and non-ortstein samples, the two sample t-test was used (Box et al., 1978). The same test was used to determine if shear strengths were significantly different among moist, air-dried, and oven-dried samples. Correlations between variables were calculated by the sample correlation formula and evaluated by a t-test (Anderson, 1958). A significance level of 0.05 was used in all cases.

Results and Discussion

Physical Analyses

Higher bulk density values were observed for ortstein horizons than for non-ortstein horizons. The differences varied from 0.12 to 0.60 Mg/m^3 (Table 4-1). The ortstein samples also had higher silt plus clay contents. As mentioned above, the paired pits opened in each county were in short distance, the parent materials and soil-forming processes were most likely the same. Thus, the higher contents of fine particles in ortstein horizons might be a result of particle translocation which may not be limited to vertical movement. An example to this effect will be discussed in Chapter VII. It is also likely that fine particles which filled the voids between coarse particles

Table 4-1. Selected chemical and physical properties of ortstein and non-ortstein spodic horizons.

Sample	B.D.+	Org. C	Particle size			Dithionite extn.		
			Sand	Silt#	Clay	Al@	Si	Fe
	Mg/m^3	-mg/g-	-------%--------			------mg/kg-----		
			Alachua					
Ort-black	1.77	19.8	90.9	6.9	2.2	3612	51	530
Ort-brown	1.58	8.3	92.1	5.2	2.7	2591	76	251
Non-ort.	1.45	9.6	94.2	4.5	1.3	1250	80	550
			Brevard					
Ort-black	1.75	28.9	92.2	2.0	5.8	4441	76	132
Ort-brown	1.71	11.3	94.1	2.8	3.1	2618	76	252
Non-ort.	1.15	20.8	96.0	0.5	3.5	1343	76	78
			St. Lucie					
Ort-black	1.73	27.3	90.2	1.9	7.9	3106	126	88
Ort-brown	1.71	15.2	92.3	2.1	5.6	2573	126	101
Non-ort.	1.59	16.2	97.7	1.1	1.2	376	10	300
			Hillsborough					
Ort.	1.65	27.3	88.2	7.3	4.5	6595	127	254
Non-ort.	1.53	10.2	93.5	3.1	3.4	1453	12	63
			St. Johns					
Ort.	1.53	45.5	96.1	0.4	3.5	4248	153	53
Non-ort.	0.97	37.4	97.7	0.5	1.8	1538	50	61

+ B.D.=Bulk density; The average bulk density of ortstein was significantly higher than that of non-ortstein samples at 0.05 significance level.

Fine particles (silt plus clay) were significantly higher in ortstein than non-ortstein samples at 0.05 significance level.

@ Average Al content was significantly higher in ortstein than non-ortstein samples, and also significantly higher than average contents of Si and Fe.

resulted in higher bulk densities of ortstein samples. The low bulk density of non-ortstein sample from St. Johns County was probably a result of high organic matter and low silt and clay contents.

The unconfined compression test is a simple test to determine the load per unit area at which the cemented specimen will fail. The differences in shear strength between moist and air-dried ortstein samples were small and not statistically significant. When the samples were oven-dried, however, the decrease of shear strength ranged from 14% for Brevard black sample to 82% for St. Johns sample (Table 4-2). The loss of water in oven-dried process might cause the dehydration of polymerized hydrated organo-metallic compounds as proposed by De Coninck (1980), therefore, decrease the strength of cementation.

In Tables 4-1 and 4-2, shear strength had no correlation with dithionite-citrate-extractable Al and bulk density probably because different samples were used for their determinations. While collapsed samples from shear strength determination were used for analyses of extractable Al (Table 4-3), the variability was eliminated and they were found to be closely related. The higher the shear strength, the more was the dithionite-citrate-extractable Al in duplicated samples from the same county. Similar relationships were found for Al extracted by pyrophosphate and oxalate except for samples from Brevard County. The

Table 4-2. Shear strength and water content (oven-dry basis) of moist (M), air-dried (A), and oven-dried (O) ortstein samples.

Samples (Layer)	H_2O			Shear strength		
	M	A	O	M+	A	O
	--------g/kg--------			-------Mg/m^2-------		
			Alachua			
Black	99.3	18.0	----	100.2	72.3	50.6
Brown	92.0	17.6	----	38.7	34.1	25.4
			Brevard			
Black	160.7	21.4	----	25.0	28.8	21.6
Brown	113.4	12.2	----	31.5	36.8	17.1
			St. Lucie			
Black	136.1	22.2	----	30.9	32.8	17.1
Brown	99.7	19.8	----	25.0	22.3	7.9
			Hillsborough			
Black	197.2	34.1	----	34.1	35.0	13.8
			St. Johns			
Black	266.0	69.7	----	36.1	23.6	6.5

+ Average shear strength of moist samples was significantly higher than that of oven-dried samples at 0.05 significance level.

Table 4-3. The relationships between shear strength and extractable Al and Fe of ortstein samples.

Soils	S.S.+	Al			Fe	Paired Diff.#	
		$S_2O_4^{2-}$	$P_2O_7^{4-}$	$C_2O_4^{2-}$	$S_2O_4^{2-}$	S.S.	Al@
	kg/cm^2	mg/kg				kg/cm^2	mg/kg
				Alachua			
Black	13.2	6375	4800	6650	725		
	9.1	4850	3250	5125	275	4.1	1525
Brown	4.9	4565	3500	5250	550		
	3.9	4275	3000	4200	145	1.0	290
				Brevard			
Black	3.5	5000	3300	4700	78		
	2.5	4500	3850	5000	78	1.0	500
Brown	3.4	3250	2400	3550	275		
	2.2	2750	2400	3350	193	1.2	500
				St. Lucie			
Black	3.2	4225	4100	4250	78		
	2.1	3525	2600	4000	76	1.1	700
Brown	3.5	4800	3150	5000	75		
	2.1	3875	2850	4900	70	1.4	925
				Hillsborough			
Black	4.1	8500	7100	9250	575		
	3.4	8000	7000	8850	375	0.7	500
				St. Johns			
Black	5.2	7000	5550	7050	50		
	3.6	5500	4450	5250	48	1.6	1500

+ S.S.=Shear strength.
# Paired difference is the difference in shear strength or extractable Al between duplicated samples. The differences of shear strength were significantly correlated with those of dithionite-citrate-extractable Al but not with those of Al from the other extractants and extractable Fe at 0.05 significance level.
@ Dithionite-citrate-extractable Al

correlation between paired differences of shear strength and those of dithionite-citrate-extractable Al (r=0.76) was significant, but not significant for the Al from the other two extractants. In the same study, dithionite-citrate-extractable Si and Fe contents which average 203 and 230 mg/kg, respectively, were much lower than those of Al and no significant correlation was found between shear strength and the extractable Si and Fe. The results suggested that Al was the main mineral element in cementing materials.

Chemical Analyses

Table 4-1 shows that at least twice as much dithionite-citrate-extractable Al was obtained from ortstein samples as from non-ortstein samples. Since dithionite-citrate is a poor reagent in extracting Al from crystalline Al hydroxides, silica, and layer silicates (Wada, 1977), the consistently and significantly higher Al contents in ortstein samples suggests that Al must have been mostly in non-crystalline forms and played an important role in cementation. The higher Al contents may also have contributed to the higher bulk density of cemented samples.

The amounts of extractable Si and Fe were always much smaller than those of Al. Ortstein samples from St. Lucie, Hillsborough, and St. Johns Counties showed a higher Si content than non-ortstein samples, but such differences were

not observed between samples from Alachua and Brevard Counties. Iron contents were generally low (Table 4-1). They were higher in ortstein than non-ortstein samples from Brevard, and Hillsborough Counties, but not for those from Alachua, St. Johns, and St. Lucie Counties.

Yuan (1969) found that the Si content was considerably lower in the spodic than other horizons in the Spodosols even though the NaOH reagent he used could have dissolved some poorly crystallized or disordered layer silicates. The dithionite-citrate-extractable Si values in this study were also low. Since this reagent is not likely to attack silicate clays as suggested by Wada (1977) and the fact that there was no correlation between clay content and dithionite-citrate-extractable Si, Si did not seem to be an important constituent for cementation.

Compared to the ortstein samples studied in Belgium by De Coninck (1980), in Canada by Miles et al. (1979), and in Soviet Union by Polteva and Sokolova (1967) and Karavayeva (1968), the Fe content in selected Florida Spodosols was quite low. This was one of typical characteristics of Haplaquods, and may be attributed to the wet conditions, under which Fe was reduced to the mobile form and then depleted following water movement. A similar finding was observed in the poorly-drained ortstein horizons in Canada (Miles et al., 1979). The fact that there was no consistent difference in Fe and Si between ortstein and non-ortstein

spodic horizons and that their amounts were small suggested that these two elements might play at most a minor role in cementation.

Organic C was lower in non-ortstein samples than in the black layers of ortstein but slightly higher than in the dark-reddish brown layers. In another study (Chapter V), fulvic acids were found significantly and consistently higher in ortstein than non-ortstein horizons. Their relation with Al in the cementation of spodic horizon will be discussed in Chapters VI and VII.

Microprobe Analyses

Results of microprobe analysis were similar for samples taken from different counties. Therefore, only the electron micrographs of samples from Alachua (northcentral Florida), Hillsborough (westcentral), and St. Lucie (eastcentral) Counties, representing different geographic locations, are presented. The energy-dispersive spectra, Figs. 4-1A and 4-1B, showed Si and Al being the dominating elements in both ortstein and non-ortstein samples, although the Al peak was weaker for non-ortstein samples under the same analytical conditions. While Fe and Mn were identified as cementing materials in ortstein by other workers (Polteva and Sokolova, 1967; Karavayeva, 1968), only relatively small or trace amounts were found in the Aquods of this study. The

epoxy resin used to impregnate the samples did not seem to affect the elemental analysis of the soil samples (Fig. 4-1A).

Distribution of Si and Al in electron-dot pictures showed that Si appeared largely on the surface of mineral particles (Figs. 4-2C, 4-2G, and 4-2K; 4-4C, 4-4G, and 4-4K;4-6C and 4-6G) but Al seemed to exist between the particles (Figs. 4-2D, 4-2H, and 4-2L; 4-4D, 4-4H, and 4-4L; 4-6D and 4-6H). Electron dots of Fe were too few to be recognized at both locations because of its low concentration. It is shown that the electron-dot density in the center of the electron-dot pictures was higher than the surrounding areas, a result caused by the electron beam focusing on that area. When the electron scan covered only a small area or a higher magnification (Figs. 4-3B and 4-3C; 4-5C and 4-5D; 4-7B and 4-7C), electron-dot density appeared more uniform. Little difference was found in distribution patterns of Al and Si between particles of ortstein (Figs. 4-2C-D and 4-2G-H; 4-4C-D and 4-4G-H; 4-6C-D) and non-ortstein (Figs. 4-2K-L; 4-4K-L; 4-6G-H) samples. However, when a lower magnification was used, it was obvious that more cementing materials and fewer voids were present between the particles of ortstein than those of non-ortstein samples (Figs. 4-2A and 4-2E vs. 4-2I; 4-4A and 4-4E vs. 4-4I; 4-6A vs. 4-6E). This probably explains the larger amounts of dithionite-citrate-extractable Al, higher silt

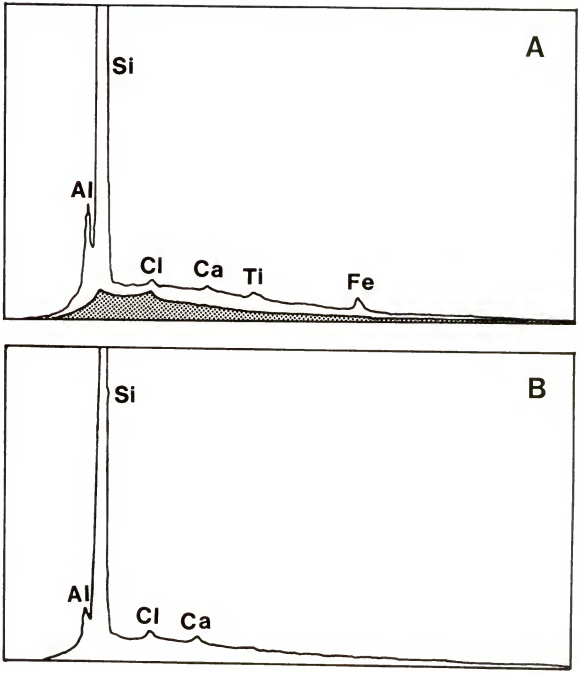


Fig. 4-1. Energy-dispersive spectra showing the elements in epoxy resin and in samples from Alachua County. (A) Epoxy resin (shaded area) and ortstein sample (corresponding to Fig. 4-2F), area analyzed approx. 250 µm x 320 µm. (B) Non-ortstein sample (corresponding to Fig. 4-2J), area analyzed approx. 250 µm x 320 µm.

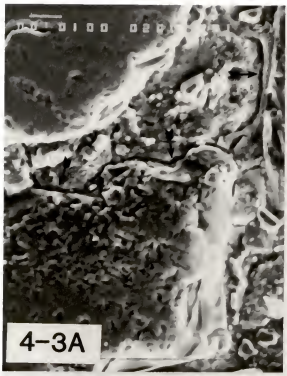
Fig. 4-2. Scanning electron micrographs showing the cementing materials between particles (4-2A, 4-2E, 4-2I) along with corresponding magnification of each micrograph's central area (4-2B, 4-2F, 4-2J), and corresponding electron-dot pictures showing the distribution of Si (4-2C, 4-2G, 4-2K) and Al (4-2D, 4-2H, 4-2L) in ortstein (4-2A to 4-2D:upper layer; 4-2E to 4-2H:lower layer) and non-ortstein samples (4-2I to 4-2L) from Alachua County. Magnification: 4-2A, 4-2E, 4-2I (130X), all others (360X). The white bars indicate 100 µm.

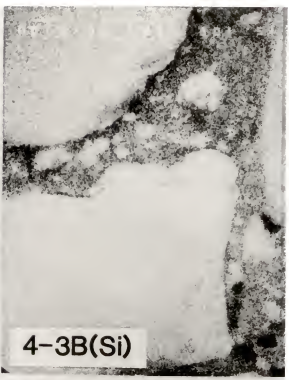
4-2A
4-2B
4-2C(Si)
4-2D(Al)

4-2E
4-2F
4-2G(Si)
4-2H(Al)

4-2J
4-2I
4-2L(Al)
4-2K(Si)

Fig. 4-3. Scanning electron micrographs and electron-dot pictures of high magnification (corresponding to the area outlined in Fig. 4-2F; magnification: 4-3A, 4-3B, 4-3C: 1000X; 4-3D: 2600X) showing Al-dominated gel-like materials, fine particles between the coarse particles, and cracks (arrowed) between the gel-like materials and coarse particles. The white bars indicate 10 μm.


4-3A


4-3B(Si)

4-3C(Al)

4-3D

Fig. 4-4. Scanning electron micrographs showing the cementing materials between particles (4-4A, 4-4E, 4-4I) along with corresponding magnification of each micrograph's central area (4-4B, 4-4F, 4-4J), and corresponding electron-dot pictures showing the distribution of Si (4-4C, 4-4G, 4-4K) and Al (4-4D, 4-4H, 4-4L) in ortstein (4-4A to 4-4D:upper layer; 4-4E to 4-4H:lower layer) and non-ortstein samples (4-4I to 4-4L) from St. Lucie County. Magnification: 4-4A, 4-4E, 4-4I (130X), all others (360X). The white bars indicate 100 μm.

4-4A
4-4B
4-4C(Si)
4-4D(Al)

4-4E
4-4F
4-4G(Si)
4-4H(Al)

4-4I
4-4J
4-4K(Si)
4-4L(Al)

Fig. 4-5. Scanning electron micrographs and electron-dot pictures of high magnification (corresponding to the area outlined in Fig. 4-4F; magnification: 4-5A: 800X; 4-5B, 4-5C, and 4-5D: 1800X) showing Al-dominated gel-like materials, fine particles between the coarse particles, and cracks (arrowed) between the gel-like materials and coarse particles. The white bars indicate 10 μm.

4-5A
4-5B
4-5C(Si)
4-5D(Al)

Fig. 4-6. Scanning electron micrographs showing the cementing materials between particles (4-6A, 4-6E) along with corresponding magnification of each micrograph's central area (4-6B, 4-6F), and corresponding electron-dot pictures showing the distribution of Si (4-6C, 4-6G) and Al (4-6D, 4-6H) in ortstein (4-6A to 4-6D) and non-ortstein samples (4-6E to 4-6H) from Hillsborough County. Cracks (arrowed) between the gel-like materials and coarse particles are also shown in Figs. 4-6A and 4-6B. Magnification: 4-6A, 4-6E (130X), all others (360X). The white bars indicate 100 μm.

4-6A
4-6B
4-6C(Si)
4-6D(Al)

4-6E
4-6F
4-6G(Si)
4-6H(Al)

Fig. 4-7. Scanning electron micrographs and electron-dot pictures of high magnification (corresponding to the area outlined in Fig. 4-6B; magnification: 4-7A, 4-7B, and 4-7C: 1800X) showing Al-dominated gel-like materials, fine particles between the coarse particles. The white bars indicate 10 μm.

4-7A
4-7B(Si)
4-7C(Al)

plus clay contents, and higher bulk density values for ortstein samples (Table 4-1).

The scanning-electron micrographs of higher magnification (Figs. 4-3A and 4-3D; 4-5A and 4-5B; 4-7A) showed that the spaces between soil particles were filled with fine particles (<20 μm) and gel-like substances, both of which probably acted as cementing agents. The accompanying electron-dot pictures (Figs. 4-3B and 4-3C; 4-5C and 4-5D; 4-7B and 4-7C) indicated that Al was the dominant element of the gel-like substances. Silicon was also present, but its density was much less than that of Al as supported by low levels of dithionite-citrate-extractable Si (Table 4-1). The presence of Si in the cementing material may be attributed to : (1) Dissolved Si originally present in this area, and (2) Si introduced by contamination due to "smearing" during the grinding process in sample preparation. Although most of the Si from the latter source may have been removed during polishing stage with diamond paste, such contamination was still possible.

The electron micrographs (Figs. 4-3A and 4-3D; 4-5A and 4-5B; 4-6A and 4-6B) also showed cracks in gel-like cementing materials between particles. The cracks may have been resulted from shrinkage of the gel-like materials in the heating process during impregnation of sample with epoxy resin. The sparse Si electron dots appeared in cracked area (Figs. 4-3B, 4-5C, and 4-7B) might be a result of

contamination from the smearing effect. De Coninck (1980) attributed the cracks in his study to the transition of the gel into a solid state by dehydration. The formation of cracks may explain the decrease in shear strength of oven-dried samples. The nature of the gel-like materials is not yet known. However, results of a separate study (Chapter V) showed strong evidences that they were predominantly Al-organic matter complexes.

From the above results, it seems that both Al-dominated gel-like substances and fine particles are involved in cementation of spodic horizons. They are analogous to cement and sand, in the making of commercial concrete, in holding the coarse particles tightly together. The amounts of these materials and their relative proportions also are important. The conditions under which ortstein is formed are yet to be understood.

CHAPTER V
DIFFERENCES IN CHEMICAL, PHYSICAL, AND CLAY MINERALOGICAL PROPERTIES BETWEEN ORTSTEIN AND NON-ORTSTEIN SPODOSOLS

Introduction

In the previous electron microprobe study (Chapter IV), cementing materials in ortstein samples were identified as a mixture of Al-dominated gels and very fine soil particles. Although the microprobe is a valuable tool for visual identification of major constituents, it can not be applied to elements of atomic number lower than nine (Reed, 1975). Therefore, it is still not known whether the Al-dominated gel-like substances were organic complexes, hydrous oxides, and/or non-crystalline Al silicates (Flach et al., 1969; Miles et al., 1979; De Coninck, 1980; McKeague and Wang, 1980; Farmer et al., 1984). An attempt was made to differentiate Al forms chemically.

Sodium-pyrophosphate at 0.1 M concentration has been used as a selective extractant for Al and Fe in soil organic complexes (McKeague, 1967; Childs et al., 1983; Farmer et al., 1983). Acid NH_4-oxalate, dithionite-citrate, and 0.5 M NaOH solutions have also been suggested to be good for extraction of organo-metallic complexes from soils (Wada,

1977; Scheldrick, 1984). In addition, NH_4-oxalate has been commonly used for dissolving non-crystalline inorganic Fe and Al, dithionite-citrate for non-crystalline Al and both non-crystalline and crystalline inorganic Fe oxides, and 0.5 M NaOH for Al and Si in non-crystalline and some crystalline forms in soils. The extraction of soil Al, Fe, and Si by these reagents, individually or in combination with pyrophosphate, may shed some light on the form or forms of gel-like substances in ortstein.

In addition to an attempt for possible identification of Al-dominated gel-like substances, chemical, physical, and clay mineralogical characteristics of ortstein and non-ortstein Florida Spodosols were also compared.

Materials and Methods

Spodosols with and without ortstein horizons from five counties in Florida, as described in Chapter III, were used.

A slaking test was performed on ortstein clods. Large blocks of ortstein samples were cut into 2.5-cm cubes and air-dried. The cubes were then placed in 500-ml beakers on a plastic net with 0.5 cm openings and soaked in water, dithionite-citrate, 0.1 M Na-pyrophosphate, 0.2 M acid NH_4-oxalate (pH 3), and 0.5 M NaOH. Time required for complete collapse of clods through the nets was recorded.

Portions of soil samples were air-dried, mixed, and sieved through a 2-mm sieve. Soil pH was measured at a soil:water ratio of 1:1 and a soil:0.01 M $CaCl_2$ ratio of 1:2 (McLean, 1982). Organic C was determined by the dichromate oxidation method (Nelson and Sommers, 1982). The procedure proposed by Schnitzer et al. (1981) was followed to separate fulvic- and humic- acid fractions for the determination of their contents. Determinations of mineral elements extracted with dithionite-citrate, Na-pyrophosphate, and acid NH_4-oxalate were made following the procedures described by Scheldrick (1984). The Hashimoto and Jackson method (1960) was used for the 0.5 M NaOH extraction.

In order to study chemical form or forms of gel-like substances, ortstein samples were treated with Na-pyrophosphate, followed by extraction with dithionite-citrate, acid NH_4-oxalate, or 0.5 M NaOH. Aluminum, Fe, and Si in each extract were determined.

A pipette method was used for the analysis of particle-size distribution (Day, 1965). For mineralogical analysis, soil samples of ortstein and non-ortstein spodic horizons were pretreated with chlorox and dithionite-citrate-bicarbonate to remove organic and oxide coatings. Sand was separated by wet sieving. Silt and clay were separated by centrifugation using dilute Na_2CO_3 solution at pH 10 as a dispersing agent. Clay was then mounted on unglazed ceramic tiles with regular Mg-glycerol, K, and K-heating treatments.

X-ray diffraction patterns were obtained with a General Electric XRD-700 diffractometer. Differential scanning calorimetry (DSC) was used to estimate the weight percentage of gibbsite in clay.

Results and Discussion

Analysis of ortstein and non-ortstein samples showed typical characteristics of sandy Spodosols. Ratios of pyrophosphate-extractable Al plus carbon to clay were greater than 0.2, and those of pyrophosphate-extractable Fe plus Al to dithionite-citrate-extractable Fe plus Al were greater than 0.5 (Table 5-1). These ratios met the requirements specified for spodic horizons (Soil Survey Staff, 1975).

Slaking Test

Results of the slaking test are shown in Table 5-2. Since all soil cubes were of roughly the same volume, the collapsing time might be used as an indicator of the effectiveness of each reagent in dissolving the cementing materials in ortstein. Dithionite-citrate was the most effective reagent in slaking the ortstein clods. Although the collapsing rate was slower in pyrophosphate, oxalate,

Table 5-1. Some calculated ratios used as criteria of spodic horizons and Al-organic complexes.

Soils	Al_p[@]+Org.C / Clay	Fe_p+Al_p / Fe_d+Al_d	Al_p / Al_o	Al_o / C	Max. Org. Complexes (%)
		Alachua			
Ort-black	1.05	0.87	0.78	0.22	55
Ort-brown	0.39	0.85	0.84	0.33	36
Non-ort.	0.82	0.85	0.63	0.17	71
		Brevard			
Ort-black	0.56	0.81	0.76	0.17	71
Ort-brown	0.44	0.91	1.00	0.21	57
Non-ort.	1.51	0.94	0.76	0.13	92
		St. Lucie			
Ort-black	0.38	0.90	0.92	0.11	100
Ort-brown	0.31	0.78	0.67	0.20	60
Non-ort.	1.39	1.08	1.06	0.03	100
		Hillsborough			
Ort.	0.76	1.01	0.91	0.24	50
Non-ort.	0.34	0.95	0.94	0.14	86
		St. Johns			
Ort.	1.40	0.81	0.98	0.07	100
Non-ort.	2.16	1.00	0.96	0.04	100

@ The lower-case letters: p=pyrophosphate, o=oxalate, d=dithionite-citrate.

Table 5-2. The collapsing rate (hrs.) of ortstein clods in various reagents.

Soils	Reagents			
	Oxalate	Pyrophos.	Dithio.	NaOH
Alachua-black	13.9	14.0	2.1	6.1
Alachua-brown	14.3	16.0	2.0	3.3
Brevard-black	4.0	0.2	I.C+	1.2
Brevard-brown	4.5	2.1	0.2	2.5
St. Lucie-black	42.9	0.1	I.C	1.2
St. Lucie-brown	46.1	3.8	I.C	2.3
Hillsborough	7.5	13.6	3.7	4.8
St. Johns	0.2	3.4	I.C	0.2

+ I.C=Immediately and completely collapsed.

and NaOH solutions, the specimens eventually collapsed. This indicated that the major components of cementing materials could be dissolved by these reagents. According to Wada (1977) and Miles et al. (1979), all of these solutions are effective in removing Al associated with organic matter. Ortstein samples did not slake in water.

During the slaking test, bubbles were observed in the clod-solution interfaces and on the surface of solutions, especially when dithionite-citrate and oxalate were used. Bubble production increased with time until the ortstein clods completely collapsed. The bubbles are believed to be CO_2 and SO_2 from redox reactions of Fe with oxalate and dithionite-citrate, respectively. The process may be illustrated as follows, assuming Fe to be either in $Fe(OH)_3$ form or as $Fe(OH)_2^+$ associated with organic matter (Lindsay, 1979):

In oxalate solution, the reactions are:

$$C_2O_4^{2-} + 2\ Fe(OH)_2^+ + 4\ H^+ \rightleftharpoons 2\ CO_{2(g)} + 2\ Fe^{2+} + 4\ H_2O \qquad \log K^o = 38.8$$

$$C_2O_4^{2-} + 2\ Fe(OH)_{3(soil)} + 6\ H^+ \rightleftharpoons 2\ CO_{2(g)} + 2\ Fe^{2+} + 6\ H_2O \qquad \log K^o = 51.6$$

In dithionite-citrate solution:

$$S_2O_4^{2-} + 2\ Fe(OH)_2^+ + 4\ H^+ \rightleftharpoons 2\ SO_{2(g)} + 2\ Fe^{2+} + 4\ H_2O \qquad \log K^o = 18.3$$

$$S_2O_4^{2-} + 2\ Fe(OH)_{3(soil)} + 6\ H^+ \rightleftharpoons 2\ SO_{2(g)} + 2\ Fe^{2+} + 6\ H_2O \qquad \log K^o = 31.0$$

Clay Mineralogy

Quartz, kaolinite, and hydroxy-Al interlayered vermiculite (Fig. 5-1; Table 5-3) were found in the clay fractions of most soils examined. Small amounts of smectite were also present in St. Lucie non-ortstein and St. Johns ortstein samples (Fig. 5-1c; Table 3). The hydroxy-Al interlayered mineral as defined by Zelazny and Carlisle (1971) is represented by a peak at 1.42 nm which neither collapses to 1.0 nm nor remains at 1.4 nm upon heating to 550°C (Fig. 5-1a). Quartz peaks were dominant in ortstein samples from Hillsborough and St. Johns Counties and in non-ortstein samples except the one from St. Lucie County. Peaks of kaolinite and hydroxy-Al interlayered vermiculite were strong in the samples which were not quartz-dominated. Gibbsite was found in ortstein horizons from Brevard and St. Lucie Counties and in non-ortstein horizons from Brevard, St. Lucie, Hillsborough and St. Johns Counties. Based on thermal analysis, its content was less than 5% in all samples (Table 5-3).

Chemical and Physical Properties

The five paired profiles of Spodosols had similar physical and chemical properties in comparative horizons (Tables 5-4 and 5-5).

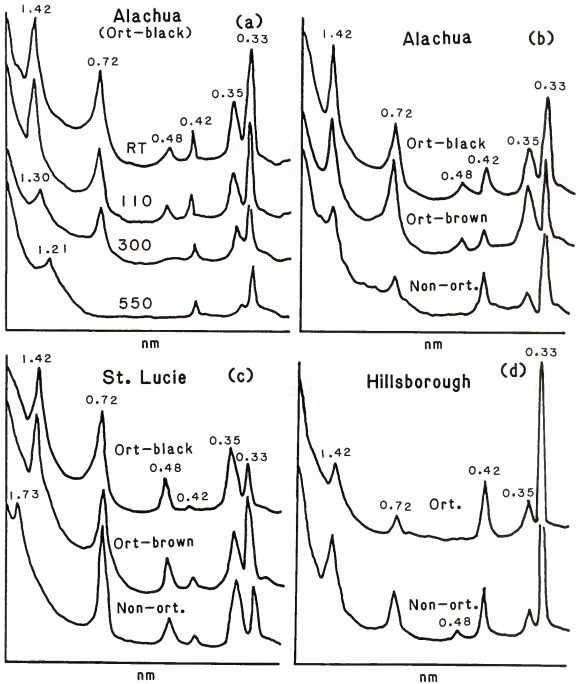


Fig. 5-1. X-ray diffractograms of (a) K-saturated clay for black ortstein horizon from Alachua County at different temperatures (^{o}C) showing hydroxy-interlayered vermiculite; (b), (c), and (d) Mg-saturated clay for ortstein and non-ortstein spodic horizons from Alachua, St. Lucie, and Hillsborough Counties, respectively.

Table 5-3. Clay mineralogical data of ortstein and non-ortstein spodic horizons.

Soils	Gibbsite[+]	Quartz[$]	Kaolinite	2:1 mineral[@]
	----%---	----------peak intensity----------		
		Alachua		
Ort-black	nf	M	M	S
Ort-brown	nf	M	S	S
Non-ort.	nf	VS	W	M
		Brevard		
Ort-black	1.3	M	M	VS
Ort-brown	2.4	M	M	VS
Non-ort.	2.0	VS	W	W
		St. Lucie		
Ort-black	5.0	W	S	S
Ort-brown	4.5	M	M	S
Non-ort.	0.7	M	S	(M)
		Hillsborough		
Ort.	nf	VS	W	W
Non-ort.	1.1	VS	M	M
		St. Johns		
Ort.	nf	VS	W	(W)
Non-ort.	0.3	VS	W	nf

+ Percentage of gibbsite weight was determined by DSC.
$ Quartz, kaolinite, and 2:1 mineral were rated on the peak intensity as VS (very strong), S (strong), M (medium), W (weak) and nf (not found).
@ 2:1 minerals are hydroxy-interlayered vermiculite except for the two in parentheses, which are smectites.

Table 5-4. Some chemical and physical properties of ortstein and non-ortstein soils.

Horizons	Depth	pH		Org. C	Particle size dist.		
		H_2O	$CaCl_2$		Sand	Silt	Clay
	--cm--			-mg/g-	----------%-------		
			Alachua (ort.)				
A	0- 30	4.2	3.2	8.6	95.4	3.4	1.2
E	30- 61	5.2	3.7	1.3	96.6	2.9	0.5
Bh1	61- 91	4.3	3.7	24.7	89.1	3.8	7.1
Bh2	91-107	4.2	3.5	29.9	91.7	2.5	5.8
Bhm1	107-122	4.3	3.6	19.8	90.7	6.9	2.2
Bhm2	122-137	4.4	3.9	8.3	92.1	5.2	2.7
C	137+	4.6	4.0	2.1	93.4	3.2	3.4
			Alachua (Non-ort.)				
A	0- 20	3.8	2.7	7.2	95.9	3.9	0.2
E	20- 51	3.9	3.0	2.1	94.6	4.7	0.7
Bh	51- 66	4.3	3.8	9.6	94.2	4.5	1.3
C	66- 89	4.5	4.2	3.6	94.8	4.2	1.0
			Brevard (ort.)				
A	0- 18	4.4	3.2	21.4	97.3	0.1	2.6
E	18- 51	4.8	3.6	2.8	98.2	0.2	1.6
Bh	51- 56	4.0	3.2	55.6	94.4	0.6	5.0
Bhm1	56- 70	4.1	3.4	28.9	92.2	2.0	5.8
BhM2	70- 81	4.4	3.8	11.3	94.1	2.8	3.1
C	81- 97	4.5	4.1	3.9	95.7	0.8	3.5
			Brevard (non-ort.)				
A	0- 18	4.2	3.1	20.8	97.6	1.3	1.1
E	18- 51	4.7	3.5	3.2	96.8	2.3	0.9
Bh1	51- 61	4.0	3.2	50.5	96.0	0.5	3.5
Bh2	61- 74	4.2	3.7	20.8	94.5	0.9	4.6
C	74- 91	4.3	4.0	7.3	94.2	1.2	4.6

Table 5-4--Continued.

Horizons	Depth	pH		Org. C	Particle size dist.		
		H_2O	$CaCl_2$		Sand	Silt	Clay
	--cm--			-mg/g-	----------%-------		
			St. Lucie (ort.)				
A	0- 18	4.6	3.8	4.2	97.7	1.3	1.0
E	18- 51	4.4	4.0	0.5	98.5	1.3	0.2
Bh	51- 56	4.5	3.6	13.1	90.2	8.8	1.0
Bhm1	56- 75	4.7	3.9	27.3	90.3	1.9	7.9
Bhm2	75- 86	4.9	4.1	15.2	92.3	2.1	5.6
E'	86-102	4.8	4.1	1.6	96.5	1.3	2.2
Btg	102+	4.7	4.0	3.8	81.5	0.9	17.6
			St. Lucie (non-ort.)				
A	0- 15	4.7	3.5	12.2	95.9	1.0	3.1
E	15- 56	5.6	4.5	1.0	98.7	0.3	1.0
Bh	56- 71	5.1	4.4	16.2	97.7	1.1	1.2
Btg	71+	5.5	5.0	7.6	81.8	1.3	16.9
			Hillsborough (ort.)				
A	0- 15	4.9	3.8	8.6	95.8	2.3	1.9
E	15- 19	6.5	5.9	0.4	97.7	1.0	1.3
Bh	69- 71	4.9	4.0	11.8	84.2	14.7	1.1
Bhm	71- 99	4.4	3.8	27.3	88.2	7.3	4.5
C	99+	4.8	4.3	14.6	89.4	6.5	4.1
			Hillsborough (non-ort.)				
A	0- 15	4.9	4.0	18.7	95.0	2.8	2.0
E	15- 66	5.4	4.4	0.8	97.3	1.0	1.7
Bh	66- 76	4.7	3.9	10.2	93.5	3.1	3.4
C	76+	4.6	3.9	10.2	95.6	2.8	1.6

Table 5-4--Continued.

Horizons	Depth	pH		Org. C	Particle size dist.		
		H_2O	$CaCl_2$		Sand	Silt	Clay
	--cm--			-mg/g-	----------%-------		
			St. Johns (ort.)				
A	0- 15	3.9	3.1	38.7	96.2	0.2	3.6
E	15- 81	4.8	3.7	1.9	98.7	0.5	0.8
Bh	81-137	4.0	3.2	16.1	97.8	1.3	0.9
Bhm	137-168	4.2	3.4	45.5	96.1	0.4	3.5
C	168+	4.4	3.4	5.3	99.2	0.6	0.2
			St. Johns (non-ort.)				
A	0- 15	4.0	3.1	53.3	90.5	4.9	4.6
E	15- 86	4.9	3.7	1.5	98.8	1.1	0.1
Bh	86-109	4.2	3.4	37.4	97.7	0.5	1.8
C	109-137+	4.3	3.4	4.3	99.0	0.9	0.1

Table 5-5. Extractable Al, Fe, Si and Mn in soil profiles by dithionite-citrate, oxalate, pyrophosphate, and NaOH .

Soils	Horizons	Al_d+	Al_p	Al_o	Al_n	Fe_d	Si_d	Mn_d
		----------mg/kg----------						
				Alachua				
Ort.	A	125	112	100	210	83	476	4
	E1	25	20	20	40	28	75	3
	Bh1	2922	2681	2872	3060	58	50	3
	Bh2	2308	2145	2363	3904	70	25	2
	Bhm1	3612	3250	4293	5550	530	51	3
	Bhm2	2591	2275	2717	4875	251	75	3
	C	1028	1000	1203	1700	113	75	2
Non-ort.	A	150	100	163	185	73	210	2
	E	43	40	78	70	58	50	2
	Bh	1250	1000	1600	2875	550	90	2
	C	575	485	1325	910	228	75	2
				Brevard				
Ort.	A	100	60	50	130	78	250	3
	E	25	15	20	25	25	50	2
	Bh	2826	2540	2725	3252	172	76	3
	Bhm1	4441	3625	4771	4736	132	76	3
	Bhm2	2618	2425	2417	2624	252	76	2
	C	1203	850	1102	1270	677	50	2
Non-ort.	A	125	55	50	125	105	275	2
	E	25	20	20	25	40	50	2
	Bh1	2343	2225	2266	2551	113	76	3
	Bh2	2290	2025	2668	2994	78	76	2
	C	2208	1600	2108	2631	452	50	2
				St. Lucie				
Ort.	A	75	45	50	85	40	175	3
	E	25	8	20	30	30	50	2
	Bh	351	200	250	400	53	50	2
	Bhm1	3106	2825	3081	2900	88	126	4
	Bhm2	2573	2025	3045	4600	101	126	3
	E'	225	100	252	260	35	25	2
	Btg	479	350	554	545	328	100	2

Table 5-5--Continued.

Soils	Horizons	Al_d+	Al_p	Al_o	Al_n	Fe_d	Si_d	Mn_d
		mg/kg						
				St. Lucie				
Non-ort.	A	75	50	70	100	301	225	3
	E	75	50	70	100	300	25	3
	Bh	376	475	450	750	802	10	2
	Btg	278	160	404	480	883	76	2
				Hillsborough				
Ort.	A	200	125	150	210	60	200	3
	E	25	10	20	25	23	25	2
	Bh	676	300	601	700	275	0	2
	Bhm	6595	6125	6696	6850	254	127	3
	C	4837	4400	5113	5024	108	176	3
Non-ort.	A	400	250	350	460	118	175	3
	E	25	10	20	30	23	0	2
	Bh	1453	1325	1403	1700	63	10	2
	C	1579	1300	1804	1800	50	50	2
				St. Johns				
Ort.	A	151	100	151	180	131	201	3
	E	25	10	20	13	25	50	2
	Bh	351	400	350	375	43	50	2
	Bhm	4248	3400	3457	4640	53	153	3
	C	200	200	150	260	38	50	2
Non-ort.	A	278	200	202	260	141	454	3
	E	25	10	20	25	60	50	2
	Bh	1538	1500	1563	1760	61	50	3
	C	75	50	50	63	33	25	2

+ The lower-case letters: p=pyrophosphate, o=oxalate, d=dithionite-citrate. n=NaOH,

All soils were acidic. Most of the horizons had a pH below 5 (Table 5-4). Spodic horizons contained more organic C than surface horizons except for non-ortstein soils from St. Johns County, and ortstein horizons more than non-ortstein. Within the ortstein horizons, black layers had a higher organic C value than dark reddish-brown layers. Spodic horizons are characterized by illuvial accumulation of amorphous materials including organic matter and hydrous Al and/or Fe oxides. Petersen (1976) suggested that, in podzolization, organic C may be translocated and accumulated in spodic horizons as metal-organic complexes.

Particle size distribution showed that most samples contained more than 90% sand (Table 5-4), except those from the Btg horizon of St. Lucie Spodosols and from the B and C horizons of Hillsborough ortstein soils. Fine-particle (silt and clay) contents were higher in subsurface horizons except for non-ortstein soils from St. Johns County. More fine particles were found in ortstein horizons than in corresponding Bh horizons of non-ortstein soils, indicating a greater eluviation of fine particles from surface layers. The results were in agreement with those found in selected non-ortstein Florida Spodosols (Pettry et al., 1965; Carlisle and Schoon, 1969; Zelazny and Carlisle, 1971).

Quantities of extractable Al were much larger than those of Fe, Si, and Mn (Table 5-5). In most soils, sodium hydroxide extracted the largest amounts of Al while

pyrophosphate extracted the least. This was attributed to the fact that NaOH may dissolve gibbsite and poorly crystalline mineral constituents, while pyrophosphate is a poor reagent for Al other than Al-organic complexes (Wada, 1977).

In each ortstein soil profile, there was a loose, dark horizon (Bh, 10YR 2/1) overlying the ortstein horizon (Bhm). These horizons were high in organic C, silt and clay, and extractable Al. Such horizons might be developed from the illuviation of these materials due to low permeability of underlying ortstein horizons.

Manganese content was too low (<4 mg/kg in all samples) to act as a cementing agent. This is contrary to that found for selected Soviet Spodosols (Polteva and Sokolova, 1967).

Silicon content was the highest in the surface among the four elements analyzed (Table 5-5). On the other hand, Al was the highest in spodic horizons as was shown by Yuan (1969). This indicated that acid leaching had removed Al from the surface horizon and deposited it in the spodic horizon, while Si was left behind.

Although Fe content was much lower than that of Al, and its distribution in gel-like substances was not detectable by electron microprobe (Chapter IV), coatings of Fe caused the reddish-brown color in lower layers of ortstein from Alachua, Brevard, and St. Lucie Counties. From the fact that dithionite-citrate was the most efficient reagent in

dissolving soil Fe (Wada, 1977) and in collapsing ortstein cubes, the coatings of Fe may play only a minor role in cementation.

Chemical Forms of Gel-like Substances

Table 5-6 shows the results of Al, Fe, and Si extractable by oxalate, dithionite-citrate, and NaOH following pyrophosphate extraction. The amounts of extractable Al and Fe, in comparison with those in Table 5-5, were low in all extracts. This indicated that most Al and Fe had been extracted by pyrophosphate. Since pyrophosphate dissolves more specifically organic Al and Fe complexes (McKeague, 1967; Childs et al., 1983; Farmer et al., 1983), most of these elements in the gel-like substances must be in organic-complex form. This conclusion is in agreement with that from the slaking test.

The ratio of pyrophosphate-extractable Al (Al_p) to oxalate-extractable Al (Al_o) had been used to indicate the proportion of organic-bound Al in total Al translocated from the surface (Childs et al, 1983). The Al_p/Al_o ratios shown in Table 5-1 indicate that more than 75% of the Al in ortstein horizons existed as organic complexes except for the reddish-brown layer from St. Lucie County.

Table 5-6. Extractable Al, Fe, and Si by oxalate, dithionite, and NaOH following pyrophosphate extraction.

layers	oxalate			dithionite			NaOH		
	Al	Fe	Si	Al	Fe	Si	Al	Fe	Si
	mg/kg								
				Alachua					
black	200	12	tr+	72	20	35	376	tr	400
brown	252	20	tr	140	50	50	600	tr	650
				Brevard					
black	80	20	tr	32	16	50	220	tr	300
brown	160	30	tr	120	30	75	600	tr	350
				St. Lucie					
black	252	10	tr	52	10	50	600	tr	200
brown	100	12	tr	72	20	99	650	tr	150
				Hillsborough					
black	112	10	tr	100	20	50	100	tr	250
				St. Johns					
black	40	10	tr	40	20	75	60	tr	100

+ Trace amounts.

Higashi et al. (1981) declared that pyrophosphate might also extract amounts of Fe and Al not bound to organic matter. Their study suggested that soil organic matter could probably not bind Al and Fe in atomic ratio of (Al+Fe)/C greater than 0.12. Using this value and disregarding the low Fe contents, the ratios of oxalate-extractable Al to dichromate-oxidizable C (Table 5-1) showed that more than 50% of the Al was complexed with organic matter except for the lower layer from Alachua County. If total C were used, the Al_o/C ratios will be lower and the percentage of Al-organic matter complexes would be higher.

Farmer et al. (1984) claimed that acid NH_4-oxalate was a selective, quantitative solvent for allophane and imogolite. Based on this, they found that proto-imogolite allophane was the principal cementing agent of Australian ortsteins. However, the trace amounts of oxalate-extractable Si and Al remaining in our samples after pyrophosphate extraction (Table 5-6) indicated that proto-imogolite allophane, though found as a cementing agent in Australian Spodosols, did not exist in Florida ortsteins.

All of the above results provide strong evidence that Al-organic matter complexes were the dominant form of gel-like substances in Florida ortsteins studied. The results were consistent with those reported for selected Spodosols in Canada (Miles et al., 1979; McKeague and Wang, 1980).

CHAPTER VI
CHARACTERIZATION OF ORGANIC MATTER AND GENESIS OF ORTSTEIN SPODOSOLS IN FLORIDA

Introduction

In previous studies, we found that gel-like cementing substances in ortstein and non-ortstein spodic horizons existed predominantly as Al-organic matter complexes. Characterization of organic matter may help to understand the nature of cementing materials.

It is known that fulvic acids are more reactive, and thus more effective in complexing metals, than humic acids. Fulvic acids also have higher acidities and lower molecular weight than humic acids, thus, the metal complexes of fulvic acids are more soluble than those of humic acids (Gieseking, 1975; Stevenson, 1982). The properties and relative amounts of fulvic and humic acids may be used to study the predominant form of Al-organic matter complexes. In addition, the C/N ratio and that of extinction coefficients at 465 and 665 nm referred to as the E_4/E_6 ratio have been widely used for characterization of organic matter (Schnitzer and Khan, 1978; Stevenson, 1982). The principal

objectives of this study are to determine C and N contents and ratios of C/N and E_4/E_6 in the organic fractions.

Materials and Methods

The soils from surface and both ortstein and non-ortstein spodic horizons used in this study were described in Chapter III.

Organic matter was characterized following the procedures proposed by Schnitzer et al. (1981). A 0.1 M pyrophosphate-0.5 M NaOH combined reagent was used for the extraction. To separate the alkaline extract from the residual soil and fulvic from humic acids, centrifugation at 14000 rpm for 20 min was used. Light absorbances by the organic fractions of pH 9 were measured at 465 and 665 nm by a Bausch & Lomb Spectronic 20 spectrophotometer and E_4/E_6 ratios were calculated. Total N and organic C were determined by the Kjeldahl method and dichromate oxidation method, respectively (Nelson and Sommers, 1982; Bremner and Mulvaney, 1982).

Results and Discussion

Optical Properties of Fulvic and Humic Acids

The E_4/E_6 ratios of aqueous fulvic and humic solutions have been widely used for the characterization of these materials. Chen et al. (1977) found that the ratios were mainly governed by the particle size but not directly related to the relative concentration of condensed aromatic rings suggested by Kononova (1966). The E_4/E_6 ratios of humic acids were all lower than those of fulvic acids (Table 6-2). This agreed with the characteristics of humic acids which have higher molecular weight and C content but lower O content and E_4/E_6 ratios than fulvic acids (Schnitzer and Desjardins, 1962; Schnitzer, 1965; Chen et al., 1977; Schnitzer and Khan, 1978). However, the values seemed to be slightly higher than those found by other workers (Stevenson, 1977; Schnitzer, 1978), probably because a high speed centrifuge was used in the separation processes (Schnitzer et al., 1981).

Carbon and N of Fulvic and Humic Acids and Their Ratios

Table 6-1 shows that ortstein had more fulvic acid-C than non-ortstein spodic horizons. The humic acid-C content

was higher in non-ortstein spodic horizons except for those samples from Hillsborough and St. Johns Counties. Ortstein also had higher fulvic acid-C to humic acid-C and fulvic acid-C to extractable C ratios than did non-ortstein spodic horizons. The ratios of fulvic acid-C to extractable C indicated that more than 75% of the extractable C in ortstein samples might have been in complex forms with Al as Al-fulvate with the exception of those in the black layer from St. Lucie County and the one from St. Johns County.

It has been pointed out and discussed in Chapters IV and V that organic C was higher in the black but lower in the dark-reddish brown ortstein than non-ortstein samples. In this study, fulvic acid-C was found to be higher in ortstein than non-ortstein spodic horizons. Table 6-1 also shows that organic C is higher in black ortstein and non-ortstein spodic than their corresponding surface horizons except for the non-ortstein soils from Hillsborough and St. Johns Counties. The results indicated illuvial accumulation of organic C in the subsurface horizons and more intense leaching in ortstein than non-ortstein zones. In most soils, N was higher in surface than subsurface horizons. This was resulted by the incorporation of organic C from plant residues into surface soils (Alexander, 1977; Stevenson, 1982). When compared with the general soil C/N range of 5 to 12 (Stevenson, 1982), ratios of the Spodosols in this study were relatively high especially those of subsurface

Table 6-1. Carbon, nitrogen contents, and ratios of C/N in soils and 0.1 M NaOH-Pyrophosphate extractions of surface, ortstein, and non-ortstein spodic horizons.

Horizons	Soils			Extractions			Extn./Soils	
	C	N	C/N	C	N	C/N	C	N
	---mg/g---			----mg/g---				
				Alachua (ort.)				
A	8.6	0.99	8.7	4.1	0.24	17.1	0.48	0.24
Bhm1	19.8	0.70	28.3	17.5	0.68	25.7	0.88	0.97
Bhm2	8.3	0.36	23.1	8.2	0.34	24.1	0.99	0.94
				Alachua (non-ort.)				
A	7.2	0.46	15.7	4.1	0.24	17.1	0.57	0.52
Bh	9.6	0.73	13.2	8.5	0.51	16.7	0.89	0.70
				Brevard (ort.)				
A	21.4	1.21	17.7	8.2	0.57	14.4	0.38	0.47
Bhm1	28.9	1.11	26.0	26.0	1.02	25.5	0.90	0.92
Bhm2	11.3	0.52	21.7	11.1	0.47	23.6	0.98	0.90
				Brevard (non-ort.)				
A	20.8	1.29	16.1	8.2	0.53	15.5	0.39	0.41
Bh	20.8	1.02	20.4	16.0	0.83	19.3	0.77	0.81
				St. Lucie (ort.)				
A	4.2	0.17	24.7	2.6	0.15	17.3	0.62	0.88
Bhm1	27.3	1.06	25.8	23.6	1.04	22.7	0.86	0.98
Bhm2	15.2	0.67	22.7	11.8	0.59	20.0	0.78	0.88
				St. Lucie (non-ort.)				
A	12.2	0.83	14.7	6.6	0.39	16.9	0.54	0.47
Bh	16.2	0.75	21.6	11.8	0.62	19.0	0.73	0.83

Table 6-1--Continued.

Horizons	Soils			Extractions			Extn./Soils	
	C	N	C/N	C	N	C/N	C	N
	----mg/g---			----mg/g---				
				Hillsborough (ort.)				
A	8.6	0.80	10.8	5.5	0.47	11.7	0.64	0.59
Bhm	27.3	1.12	24.4	24.4	0.93	26.2	0.89	0.84
				Hillsborough (non-ort.)				
A	18.7	2.15	8.7	11.8	1.09	10.8	0.63	0.51
Bh	10.1	0.63	16.0	8.9	0.53	16.8	0.88	0.84
				St. Johns (ort.)				
A	38.7	2.59	14.9	21.4	1.43	15.0	0.55	0.55
Bhm	45.5	1.73	26.3	40.4	1.56	25.9	0.89	0.90
				St. Johns (non-ort.)				
A	53.3	5.80	9.2	24.6	1.98	12.4	0.46	0.34
Bh	37.4	1.67	22.4	33.3	1.33	25.0	0.89	0.80

Table 6-2. Carbon, nitrogen contents, and ratios of C/N and E_4/E_6 of fulvic (FA) and humic (HA) acids in surface, ortstein, and non-ortstein spodic horizons.

Hori-zons	Fulvic Acids				Humic Acids				$\frac{FA^+}{Ext.}$	$\frac{FA^+}{HA}$
	C	N	C/N	E_4/E_6	C	N	C/N	E_4/E_6	(C)	(C)
	---mg/g---				---mg/g--					
Alachua (ort.)										
A	1.2	0.12	10.0	8.1	2.9	0.11	26.4	3.4	0.29	0.4
Bhm1	16.1	0.57	28.2	7.4	1.4	0.11	12.7	4.9	0.92	11.5
Bhm2	7.6	0.24	31.7	13.6	0.4	0.03	16.7	5.0	0.93	19.0
Alachua (non-ort.)										
A	2.2	0.13	16.9	6.4	1.8	0.07	25.8	3.4	0.54	1.2
Bh	5.9	0.30	19.7	8.5	2.4	0.18	13.3	3.6	0.69	2.5
Brevard (ort.)										
A	4.5	0.20	25.0	11.5	3.6	0.35	10.3	3.2	0.55	1.3
Bhm1	19.6	0.68	28.8	9.3	4.5	0.29	15.5	5.9	0.75	4.4
Bhm2	9.5	0.35	27.1	15.4	0.8	0.08	10.0	5.6	0.86	11.9
Brevard (non-ort.)										
A	2.2	0.17	12.9	6.9	6.0	0.35	17.1	3.1	0.27	0.4
Bh	10.1	0.49	20.6	8.8	5.5	0.34	16.2	5.1	0.63	1.8
St. Lucie (ort.)										
A	0.5	0.08	6.2	6.5	1.1	0.05	22.0	2.9	0.19	0.5
Bhm1	12.2	0.52	23.5	9.1	9.0	0.44	20.5	6.6	0.52	1.4
Bhm2	9.5	0.42	22.6	13.2	1.7	0.10	17.0	7.7	0.81	5.6
St. Lucie (non-ort.)										
A	2.6	0.19	13.7	4.7	3.5	0.20	17.5	4.1	0.39	0.7
Bh	3.3	0.14	23.6	9.8	7.5	0.38	19.7	4.6	0.28	0.4

Table 6-2-- Continued.

Hori-zons	Fulvic Acids C	N	C/N	E_4/E_6	Humic Acids C	N	C/N	E_4/E_6	$\frac{FA^+}{Ext.}$ (C)	$\frac{FA^+}{HA}$ (C)
	---mg/g---				---mg/g--					
				Hillsborough (ort.)						
A	2.0	0.18	11.1	7.8	3.8	0.28	11.1	3.8	0.36	0.5
Bhm	20.8	0.80	26.0	5.0	2.4	0.13	18.5	4.4	0.85	8.7
				Hillsborough (non-ort.)						
A	5.1	0.41	12.4	9.0	5.9	0.63	9.4	4.7	0.43	0.9
Bh	7.1	0.37	19.2	6.7	1.5	0.12	12.5	4.7	0.80	4.7
				St. Johns (ort.)						
A	3.5	0.29	12.1	11.9	16.2	1.04	15.6	3.7	0.16	0.2
Bhm	13.7	0.42	30.2	9.4	26.5	1.05	26.2	6.3	0.34	0.5
				St. Johns (non-ort.)						
A	5.7	0.47	12.1	12.1	12.1	1.50	11.9	4.2	0.23	0.5
Bh	3.9	0.27	14.4	12.9	25.3	1.05	24.1	6.3	0.12	0.2

+ Carbon in pyrophosphate-NaOH extractions, fulvic and humic acids.

horizons. This was probably due to more intensive N losses through organic matter decomposition under high soil temperature (> 22°C), humid moisture, and alternate wet and dry season in the areas studied (Alexander, 1977). In addition, high C/N ratios might also be attributed to the trace NH_4 held by very small amounts of clay minerals (Chapter IV) in the soils studied (Stevenson, 1982). The results were in agreement with those found by Yuan (1966). The ratios of NaOH-pyrophosphate-extractable C to soil C in ortstein or non-ortstein spodic were much higher than those in the surface horizons. They were also higher in ortstein than non-ortstein spodic horizons. Since the reagent was assumed to extract humic substances in complexation with mineral elements particularly Al and Fe, it is likely that fulvic and humic acids, especially the former, were complexed with Al and accumulated in the spodic horizon as an agent for cementation as postulated in Chapter V.

CHAPTER VII
ASSESSMENT OF AMORPHOUS MATERIAL ACCUMULATION IN ORTSTEIN HORIZONS OF SELECTED FLORIDA SPODOSOLS

Introduction

In previous studies, properties and cementing materials of paired ortstein and non-ortstein Florida Spodosols from five counties were compared (Chapters IV, V, and VI). It was found that the cementing materials were composed of Al-dominated gel-like substances and fine particles. It was also found that extractable Al and fulvic acid contents were higher in ortstein than non-ortstein spodic horizons.

Since the paired Spodosols were located within 200 m from each other, except in one county where they were about 1.6 km apart. In such short distances, the parent materials and soil-forming processes for neighboring ortstein and non-ortstein spodic horizons are most likely the same. In fact, the similarity was noted in clay mineralogy (Chapter V). However, the distinct differences in fine particles, extractable Al, and fulvic acids between ortstein and non-ortstein spodic horizons, suggested that downward leaching might not be the only mechanism in Florida Spodosols. Other mechanism or mechanisms may also be involved. This study was

an attempt to verify this possibility so that the genesis of ortstein horizons in Alachua County may be postulated.

Materials and Methods

The study covered an area of 15600 m^2 in Alachua County, Florida (Fig. 7-1) where the ortstein pit for the previous studies (site C in Fig. 7-2 and Table 7-1) was located. The elevation was higher in the northeast and lower in the southwest. Samples of surface and spodic horizons were taken from the central pit and at sites every 10 m away from the pit in all four directions until no ortstein was detected. The total area of ortstein formation was about 4000 m^2. Three additional sets of samples were collected in each direction to represent non-ortstein profiles.

Soil organic C as well as the organic C in NaOH-pyrophosphate extracts, and in fulvic and humic acid fractions was analyzed by the wet-digestion method (Nelson and Sommers, 1982). Extractable Al and Si were determined following the procedures described by Scheldrick (1984). Characterization of soil organic matter followed the procedure proposed by Schnitzer et al (1981).

To test whether the average Al and organic C contents were significantly different between samples from ortstein and non-ortstein profiles, two sample t-tests were used (Box et al., 1978). Significance was determined at 0.05 level.

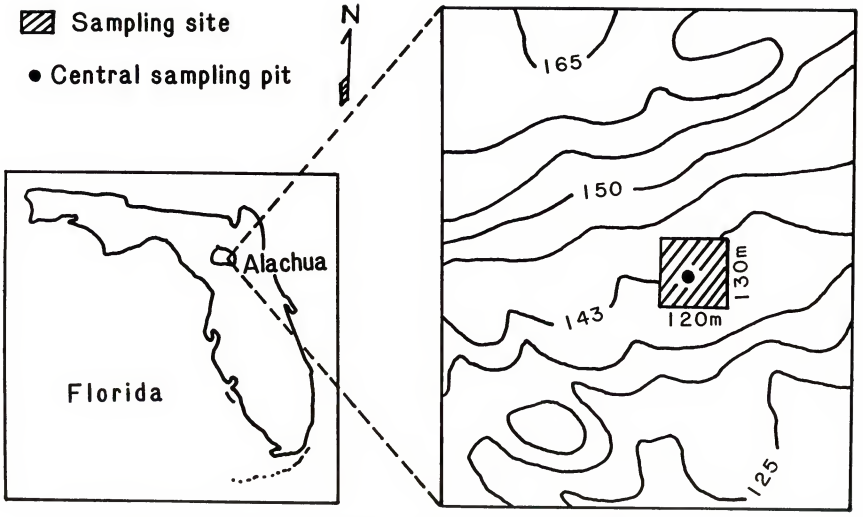


Fig. 7-1. Location and topographic map showing the elevation (m) of sampling sites in Alachua County, Florida.

Results and Discussion

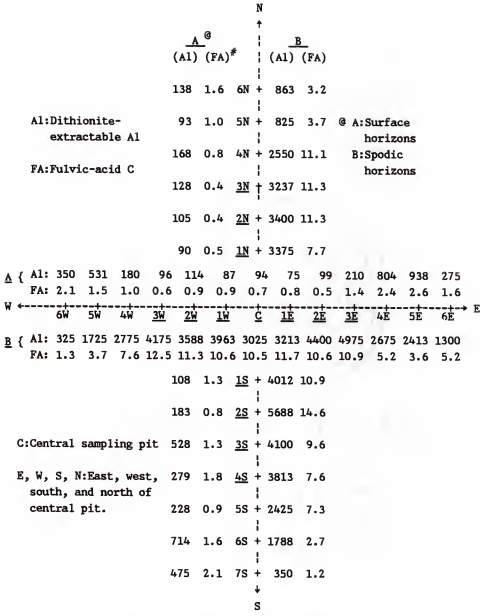
Accumulation of Al and Fulvic Acids in Ortstein Horizons

If the formation of spodic horizons is primarily a result of vertical translocation of soluble organic materials, Al, and/or Fe in the leaching process, the presence of ortstein should indicate more intense leaching. Then, less of these materials would be expected to occur in surface horizons in the ortstein area than in the non-ortstein area.

The location and topographic map of the study area are shown in Fig. 7-1. It is assumed that the soil-forming materials would likely be the same. The ortstein development occurred within the boundary of 3N to 4S, and 3E to 3W (Fig. 7-2). As postulated above, dithionite-citrate-extractable Al contents in surface horizons of ortstein sites were significantly lower than those of non-ortstein except at locations 3S and 5N (Fig. 7-2). Soil organic C and organic C in NaOH-pyrophosphate extracts as well as in fulvic and humic acid fractions showed similar trends except in the southerly direction (Table 7-1). This seemed to suggest that more intense leaching of Al and organic C had occurred in ortstein than in non-ortstein areas. The results were supported by the significantly larger amounts of Al and organic C in ortstein as compared to non-ortstein spodic

horizons (Table 7-1). Moreover, closer examination of data revealed that the average contents in 14 ortstein and 12 non-ortstein spodic horizons (Fig. 7-2) were about 3900 and 1700 mg/kg for Al and 10.8 and 4.7 mg/g for fulvic-acid C, respectively, while those in the surface horizons were only 160 and 410 mg/kg for Al, and 0.9 and 1.6 mg/g for fulvic-acid C. The difference between the average Al contents in ortstein and non-ortstein spodic horizons was 2200 mg/kg, significantly higher than the values of 250 mg/kg for surface horizons. In the meantime, the difference in fulvic-acid C between ortstein and non-ortstein soils was 6.1 mg/g for the spodic and only 0.7 mg/g for the surface horizons. These results suggested that both Al and fulvic-acid C moved down from the surface in the formation of ortstein and non-ortstein spodic horizons. Since fulvic acids are highly reactive and effective in complexing metals (Stevenson, 1982), they may have formed Al-fulvate complexes. This is consistent with the conclusion in a previous study (Chapter V) that Al-fulvate was the predominant component of cementing material. In addition, the much larger differences in both Al and fulvic-acid contents between ortstein and non-ortstein soils in the spodic than the surface horizons also suggested that Al and fulvic acids may not have totally and directly originated from the surface horizons.

If vertical translocation was not the only mechanism, lateral inflow due to topographic differences may have



Aluminum and fulvic-acid C contents were significantly higher in spodic, but significantly lower in surface horizons of ortstein than non-ortstein areas.

Fig. 7-2: Dithionite-citrate-extractable Al (mg/kg) and fulvic-acid C (mg/g) in surface, ortstein, and non-ortstein spodic horizons of sampling sites in Alachua County. Distance between two figures is 10 m. Underlined area indicates ortstein formation.

Table 7-1. Organic C in soils, NaOH-pyrophosphate extracts, and fulvic (FA) and humic acid (HA) fractions.

Locations	Surface				Spodic			
	Soil*	Extract*	HA*	FA*	Soil#	Extract#	HA	FA#
	mg/g							
C+	9.2	5.1	4.2	0.7	23.7	13.3	1.8	10.5
1E	6.5	3.8	2.7	0.8	25.6	14.7	3.0	11.7
2E	7.8	5.0	4.0	0.5	23.1	13.0	2.2	10.6
3E	15.0	9.0	6.6	1.4	24.4	13.1	2.2	10.9
4E	9.3	5.7	3.2	2.4	18.3	8.2	2.6	5.2
5E	12.9	9.0	6.2	2.6	12.2	4.9	1.4	3.6
6E	12.0	7.4	5.2	1.6	14.8	7.8	2.2	5.2
1W	7.3	4.6	3.1	0.9	19.7	11.7	1.1	10.6
2W	12.0	7.2	6.2	0.9	20.8	12.6	1.3	11.3
3W	5.6	2.7	2.1	0.6	22.5	13.9	1.3	12.5
4W	12.7	6.7	5.8	1.0	17.2	9.8	2.1	7.6
5W	7.2	4.4	2.8	1.5	11.4	5.9	2.4	3.7
6W	11.9	6.4	4.3	2.1	5.6	1.6	0.9	1.3
1S	10.1	4.8	3.2	1.3	25.1	14.4	2.5	10.9
2S	11.9	8.0	5.7	0.8	33.2	18.1	3.2	14.6
3S	10.4	6.6	4.2	1.3	24.2	12.2	2.2	9.6
4S	11.1	7.1	5.4	1.8	17.9	10.3	2.5	7.6
5S	10.8	5.7	4.8	0.9	22.8	11.7	3.3	7.3
6S	10.9	6.9	4.1	1.6	10.9	5.0	2.2	2.7
7S	11.5	8.1	5.8	2.1	9.8	4.6	3.2	1.2
1N	7.4	4.3	3.7	0.5	15.7	8.8	1.1	7.7
2N	5.8	3.5	2.5	0.4	22.6	13.7	1.7	11.3
3N	3.6	2.2	1.8	0.4	25.4	14.4	2.2	11.3
4N	15.9	11.5	10.6	0.8	24.1	15.5	4.2	11.1
5N	14.5	9.0	7.5	1.0	16.7	8.5	4.0	3.7
6N	10.5	6.7	4.9	1.6	19.4	9.3	4.9	3.6

+ C = Central pit site. E, W, S, N=East, west, south, and north of the pit, respectively. The sampling sites underlined indicate the presence of ortstein.

* Carbon contents are significantly lower in ortstein than in non-ortstein area.

\# Carbon contents are significantly higher in ortstein than in non-ortstein area.

contributed to the distinct differences in Al and fulvic-acid contents between ortstein and non-ortstein spodic horizons. This possibility was investigated by associating the variation of Al contents with the formation of ortstein in neighboring sites of Alachua Spodosols. If it is true, their contents would be expected to increase gradually from non-ortstein spodic to ortstein horizons and then to decrease gradually once more with the disappearance of ortstein. Within the sampling area, Al contents in the spodic horizon increased gradually from north to south, east to west, and then decreased. Fulvic-acid C showed a similar trend (Fig. 2). Ortstein horizons formed and then disappeared in the same direction. This indicated that considerable amounts of Al and fulvic acids in Alachua ortstein horizons might be translocated by seepage from northeast to southwest due to the differences in elevation. However, the accumulation of these materials in other Florida Spodosols is yet to be studied.

Translocation Form of Al to Ortstein Horizons

The translocation of Al and Fe from the surface of the Spodosols to the spodic horizons was suggested to be in organic complex form (Petersen, 1976; De Coninck, 1980; Stevenson, 1982). Recently, soluble Al silicate complexes were also suggested as predominant mobile forms which might

precipitate in the spodic horizon as imogolite and/or allophane (Farmer et al., 1980; Anderson et al., 1982; Childs et al., 1983). In the previous study, we found that trace amounts of allophane and imogolite existed in the gel-like cementing substances of Florida Spodosols (Chapter V). The Al and Si data from that study were recalculated and presented in Table 7-2. The Al/Si atomic ratios in the oxalate extracts of ortstein horizons from five paired Spodosols were exceedingly high except for the dark reddish-brown layer of ortstein from St. Lucie County (Table 7-2). The results did not agree with the Al/Si atomic ratio for imogolite which is 2 as suggested by Child et al. (1983). For allophane, Parfitt and Henmi (1982) recommended the use of $[100 \times Si_o(\%)]/13.3$ for estimation of its contents (%) in soil clays, if $(Al_o - Al_p)/Si_o$ is close to 2 (The lower-case letters: o=oxalate, p=pyrophosphate). By using this method, allophane is less than 1% in the ortstein and non-ortstein spodic horizons of Florida Spodosols studied (Table 7-2). The low allophane and/or imogolite contents indicated not only that these materials did not act as cementing agents but also that Al silicates were not the Al-form translocated to ortstein and non-ortstein horizons in Florida Spodosols.

As mentioned, fulvic acids are more reactive and effective in complexing Al (Stevenson, 1982). In the present study, the amount of fulvic acids in the spodic horizons increased in the ortstein area and then decreased in the

non-ortstein area, a trend similar to Al (Fig. 7-2). The values were also significantly lower in surface horizons of ortstein profiles than at non-ortstein sites, indicating possible complexation to form Al-fulvate. As supported by the chemical study (Chapter V), Al-fulvate was likely the predominant form in which Al was translocated to the spodic horizons. Therefore, Al-organic complexes were the prime agent for cementation to form ortstein.

Genesis of Ortstein Horizons

The formation of ortstein has been suggested as a chemical (or physiochemical) process or a microbiological (or biological) process (Polteva et al., 1967; Karavayeva, 1968; Sokolova and Polteva, 1968; McKeague and Wang, 1980). Regardless of the process, alternate wet and dry periods of the year and very little disruption by physical and biological forces are considered to be required conditions for cementation. Based on the results in our previous studies and in the literature, the development of ortstein in Florida Spodosols may be speculated as follows.

Aluminum, Fe, and other polyvalent cations, either as free oxides or hydroxides or as other forms from weathering of minerals, formed soluble organo-metallic complexes and were translocated and precipitated at certain depth. Spodic (Bh) horizon might be developed by the accumulation of these

Table 7-2. Oxalate-extractable Al and Si, pyrophosphate extractable Al, and some calculated results showing the low contents of allophane.

Soils	Al_o+	Al_p	Si_o	$\frac{Al_o}{Si_o}$	$\frac{Al_o - Al_p}{Si_o}$	Allophane
	------mg/kg------					----%----
			Alachua			
Ort-black	4293	3250	100	42.9	10.43	----
Ort-brown	2717	2275	150	18.1	2.95	0.11
Non-ort.	1600	1000	125	12.8	4.80	0.09
			Brevard			
Ort-black	4771	3625	900	5.3	1.27	0.68
Ort-brown	2417	2425	150	16.1	----	----
Non-ort.	2266	2025	200	11.3	1.21	0.15
			St. Lucie			
Ort-black	3081	2825	350	8.8	0.73	0.26
Ort-brown	3045	2025	1000	3.1	1.02	0.75
Non-ort.	450	475	tr	----	----	----
			Hillsborough			
Ort.	6696	6125	350	19.1	1.63	0.26
Non-ort.	1403	1325	tr	----	----	----
			St. Johns			
Ort.	3457	3400	tr	----	----	----
Non-ort.	1563	1500	tr	----	----	----

+ The lower case letters: o=oxalate, p=pyrophosphate.

materials. The immobilization or precipitation of illuviated organo-metallic complexes might be caused by any of the following mechanisms: (i) The complexes precipitated at a critical concentration level at certain depth (Boul et al., 1980); (ii) The mobility of the complexes was reduced by change of pH or Eh, or by microbial degradation of organic ligands (McKeague and Sprout, 1975; Boul et al., 1980); (iii) The complexes might be "mechanically sieved" because soil pores were clogged by fine particles (Boul et al., 1980); (iv) The complexes carried by the wetting front were stopped by water table in wet season or by deficiency of water in dry season (Fiskell and Carlisle, 1963).

Since the cementing materials consisted of Al-organic matter complexes and fine particles were more in ortstein than in non-ortstein spodic horizons, organo-metallic complexes might gradually accumulate to coat and link soil particles. In addition, fine particles translocated by leaching from the surface might link skeleton coarse grains through the action of gel-like organo-metallic complexes. In non-ortstein area, a part of Al and fulvic acid leached might move to the ortstein horizon nearby through seepage due to elevation difference. In non-ortstein area, low amounts of the complexes were accumulated, biological activity was allowed and the horizon remained loose. In ortstein area, more complexes were accumulated because of more intense leaching and the inflow of them with seepage.

The accumulation of the complexes exceeded biological activity in the horizon, cementation was gradually developed and root development was impeded (De Coninck, 1980).

CHAPTER VIII
CONCLUSIONS

A series of experiments was conducted on five pairs of ortstein and non-ortstein profiles of Florida Spodosols all classified as Aquods to study the nature of cementing materials. Significant findings may be summarized as follows:

1. Ortstein clods collapsed in dithionite-citrate, acid NH_4-oxalate, NaOH, and pyrophosphate solutions, but not in water. Among the slaking reagents, dithionite-citrate was the most effective.

2. Moist and air-dried ortstein samples had similar shear strengths, but the strength significantly decreased when samples were oven-dried. The strength had a significant correlation with the dithionite-citrate-extractable Al.

3. In the profiles, organic C, fine particles (silt plus clay), and extractable Al by dithionite-citrate, pyrophosphate, acid NH_4-oxalate, and NaOH were all higher in Bh horizons, while dithionite-citrate-extractable Si was higher in the surface horizons.

4. Ortstein horizons had significantly larger amounts of dithionite-citrate-extractable Al, higher silt plus clay

contents, and higher bulk density values than non-ortstein counterparts.

5. The amounts of dithionite-citrate-extractable Fe were much lower than those of extractable Al (< 550 mg/kg vs. > 2550 mg/kg) in ortstein horizons. Therefore, coatings of Fe on particles might play only a minor role in cementation. Manganese content was too low (< 4 mg/kg) to act as a cementing agent.

6. Energy-dispersive spectra showed that Si and Al were major constituents of both ortstein and non-ortstein samples. However, ortstein samples had stronger Al peaks.

7. More cementing materials were observed in the ortstein than non-ortstein samples in scanning electron micrographs. These cementing materials consisted of gel-like substances and fine particles. Cracks of dry gel-like substances between coarse particles were also observed.

8. Electron-dot pictures revealed that the gel-like substances were Al-dominated. Chemical analyses suggested that they were predominantly Al-fulvate.

9. Quartz, gibbsite, kaolinite, and hydroxy-Al interlayered vermiculite were dominant clay minerals in ortstein and non-ortstein spodic horizons.

Neighboring ortstein and non-ortstein sites of Spodosols from Alachua County were studied in an attempt to find possible sources of Al and fulvic acids accumulated in ortstein horizons. The studies showed the following results:

1. Extractable Al and fulvic-acid contents were significantly lower in surface horizons and significantly higher in spodic horizons at ortstein sites than in corresponding horizons at non-ortstein sites suggesting that more intense leaching had occurred in the ortstein area.

2. Differences between ortstein and non-ortstein spodic horizons in both Al and fulvic-acid contents were much higher than those between surface horizons.

3. Following the topographic difference, Al and fulvic-acid contents in Bh horizons increased from northeast to southwest, and then decreased. A similar trend was observed for the occurrence and disappearance of ortstein. The Al levels in ortstein horizons were all above 3000 mg/kg while those in non-ortstein spodic horizons were below 3000 mg/kg.

4. The findings suggested that Al and fulvic acids acting as predominant cementing agents for the ortstein horizon at Alachua County site might also have originated from seepage and translocated to the spodic horizons as a result of topographic differences.

5. Trace or no imogolite and allophane were found in ortstein and non-ortstein spodic horizons, suggesting that most Al and fulvic acids were probably translocated as Al-fulvate to these horizons.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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